Available online at www.sciencedirect.com
SCIENCE DIRECT®
Inorganica Chimica Acta 347 (2003) 114–122
Inorganica Chimica Acta
www.elsevier.com/locate/ica

tert-Butylsilylcyclopentadienyl Group 4 metal complexes

Regine Wolfgramm [a], Cristina Ramos [a], Pascual Royo [a,*], Maurizio Lanfranchi [b], Maria Angela Pellinghelli [b], Antonio Tiripicchio [b]

[a] *Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, 28871 Alcalá de Henares, Spain*
[b] *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parco Area delle Scienze 17A, I-43100 Parma, Italy*

Received 3 May 2002; accepted 12 July 2002

Dedicated to Professor R. Usón with best affection and admiration

Abstract

New Group 4 metal *t*-butyldimethylsilylcyclopentadienyl complexes [MCpCp′Cl$_2$] (Cp = η^5-C$_5$H$_5$; Cp′ = η^5-C$_5$H$_4$SiMe$_2^t$Bu; M = Ti **4**, Zr **5**, Hf **6**) were prepared by reaction of 1 equiv. of the lithium (**2**) and thallium (**3**) salts of *t*-butyldimethylsilylcyclopentadiene **1** with the monocyclopentadienyl complexes [MCpCl$_3$·DME] (M = Zr, Hf) and [TiCpCl$_3$], respectively. A similar reaction using ZrCl$_4$(THF)$_2$ and HfCl$_4$ with 2 equiv. of the lithium salt **2** gave the symmetric [MCp′$_2$Cl$_2$] (M = Zr **7**, Hf **8**) metallocenes. Alkylation of these compounds with 2 equiv. of MgRCl (R = Me, CH$_2$Ph) and Li(CH$_2$CMe$_2$Ph) afforded the dialkyl complexes [MCpCp′R$_2$] (R = Me, M = Zr **9**, Hf **10**; R = CH$_2$Ph, M = Ti **11**, Zr **12**, Hf **13**), [ZrCp′$_2$(CH$_2$Ph)$_2$] **14** and [ZrCpCp′(CH$_2$CMe$_2$Ph)$_2$] **17**. A Similar reaction of **5** with 1 equiv. of Mg(CH$_2$Ph)Cl gave the monobenzyl compound [ZrCpCp′Cl(CH$_2$Ph)] (**15**). Hydrolysis of **15** with a stoichiometric amount of water afforded the dinuclear μ-oxo compound [(ZrCpCp′Cl)$_2$(μ-O)] (**16**). All of the new complexes reported were characterized by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy and the molecular structures of **4** and **16** were determined by X-ray diffraction methods. Ethylene polymerization activities were measured for compounds **4**–**7**.

Keywords: Titanium; Zirconium; Hafnium; ^{t}Butylsilylcyclopentadienyl metallocenes; Ethylene polymerization

1. Introduction

Early transition metal cyclopentadienyl-type compounds have received special and intense research interest through their applications as Ziegler–Natta catalysts, and many articles reviewing these aspects have been published [1]. The introduction of different substituents in the cyclopentadienyl ring gives rise to significant changes in the reactivity and catalytic activity of these species [2], essentially derived from their different electronic and steric effects. Silyl substituents have been extensively used [3] with the main aim of introducing functionalized pendant moieties. We have reported many of these silyl substituted compounds which have been used more recently to stabilize cationic zirconocene species [4] by coordinating the olefinic system of a silyl–allyl substituent and to isolate new 'doubly constrained' silyl-η^1-amido complexes [5]. Formation of cationic zirconocene complexes containing benzyl and the very bulky Si(SiMe$_3$)$_3$ substituted cyclopentadienyl ligands has been studied and the role of these substituents in ethylene polymerization has been considered [6]. Bulky substituents like *tert*-butyl groups are responsible for unexpected intramolecular activation processes such as those observed for benzyl and neophyl metallocenes [7] to give metallacyclic derivatives. Similar more open cycles are easily accessible as reported for molybdenum and tungsten derivatives [8].

tert-Butylsilyl is an appropriate group to introduce the required bulkiness producing slight modifications of the electronic properties afforded by a silyl substituent. For all these reasons we decided to study the synthesis of metallocenes containing *tert*-butylsilylcyclopentadienyl ligands. Here we report the synthesis of Group 4

* Corresponding author. Tel.: +34-91-8854-765; fax: +34-91-8854-683.
E-mail address: pascual.royo@uah.es (P. Royo).

0020-1693/02/$ - see front matter
doi:10.1016/S0020-1693(02)01446-9

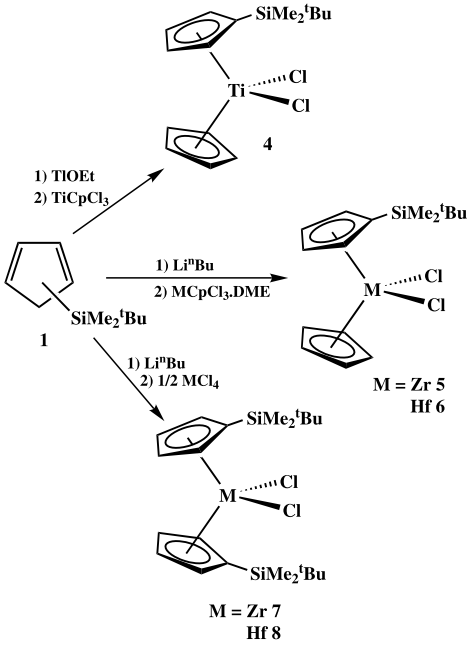
metallocenes containing this ligand, the X-ray crystal structures of the dichloro [Ti(η^5-C_5H_5)(η^5-$C_5H_4SiMe_2^tBu$)Cl_2] and the μ-oxo dinuclear [{Zr(η^5-$C_5H_4SiMe_2^tBu$)(η^5-C_5H_5)Cl]$_2$}(μ-O)] complexes and the catalyitic activity of the chloro derivatives **4**–**7** for polymerization of ethylene.

2. Results and discussion

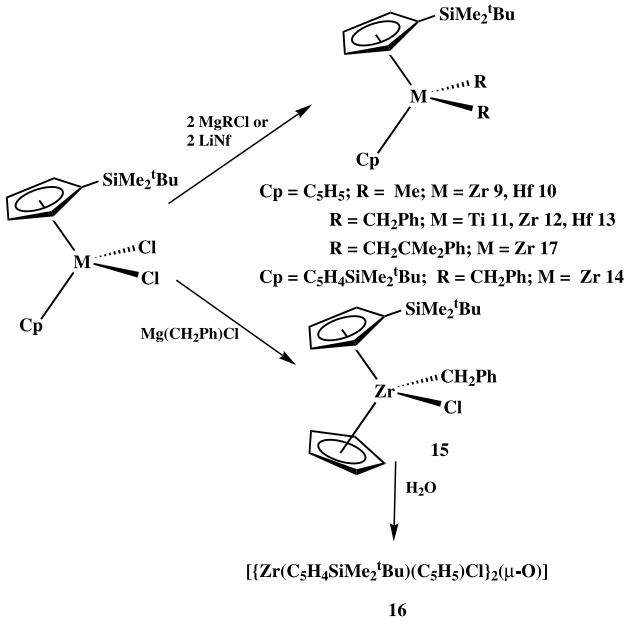
tert-Butyldimethylsilyl chloride is a usual commercial reagent extensively used as a protective group in organic synthesis [9]. Its reaction with sodium cyclopentadienide in 1/1 hexane/THF afforded the *tert*-butylsilylcyclopentadiene [$C_5H_5SiMe_2^tBu$] (**1**) which was isolated as a brown oily solid. Compound **1** was identified by ^1H NMR spectroscopy as a mixture of isomers in which the sp^3 carbon-silyl bonded cyclopentadiene is the major component in a ratio of 70%. The lithium salt Li($C_5H_4SiMe_2^tBu$) (**2**) was the most appropriate reagent to transfer the ring to zirconium and hafnium while the thallium salt Tl($C_5H_4SiMe_2^tBu$) (**3**) was a better ring transfer reagent for titanium compounds to prevent further reoxidation processes that would otherwise result in reduced products. Metallation of **1** with Li–*n*-Bu and TlOEt afforded the lithium (**2**) and thallium (**3**) salts, respectively, which were used for subsequent transfer of the *tert*-butylsilylcyclopentadienyl ligand to different Group 4 metal chlorides.

As shown in Scheme 1, reaction of the thallium salt **3** with $CpTiCl_3$ in toluene afforded the mixed dicyclopentadienyl titanium complex [Ti(η^5-C_5H_5)(η^5-$C_5H_4SiMe_2^tBu$)Cl_2] (**4**), which after recrystallization in toluene was isolated as a red solid and characterized by elemental analysis, NMR spectroscopy and X-ray diffraction methods. Similar reactions using 1 equiv. of the lithiated cyclopentadienyl ligand with the zirconium and hafnium monocyclopentadienyl complexes [$CpMCl_3 \cdot DME$] in THF gave the mixed dicyclopentadienyl dichloro complexes [M(η^5-C_5H_5)(η^5-$C_5H_4SiMe_2^tBu$)Cl_2] (M = Zr **5**, Hf **6**), isolated as beige and grey solids respectively and characterized by elemental analysis and NMR spectroscopy (see Section 4). The symmetric di(*tert*-butyldimethylsilylcyclopentadienyl) zirconium complex [Zr(η^5-$C_5H_4SiMe_2^tBu$)$_2Cl_2$] (**7**) was isolated as a beige solid from the reaction of 2 equiv. of the lithiated cyclopentadienyl ligand **2** with $ZrCl_4(THF)_2$ in THF. Similar reaction with $HfCl_4$ in THF gave, after evaporation and extraction into toluene, the symmetric dicyclopentadienyl hafnium complex [Hf(η^5-$C_5H_4SiMe_2^tBu$)$_2Cl_2$] (**8**) which was isolated as a grey solid. Both compounds are soluble in toluene and scarcely soluble in hexanes and were characterized by analyses and NMR spectroscopy.

As shown in Scheme 2, the mixed metallocene dichlorides **4**–**6** were straightforwardly transformed into the dialkyl derivatives by reaction with the corresponding alkylating agents. Pure samples of neither the mono nor the dimethyltitanium complexes could be obtained using different molar ratios of MgMeCl, whereas the dimethyl complexes [M(η^5-C_5H_5)(η^5-$C_5H_4SiMe_2^tBu$)Me_2] (M = Zr **9**, Hf **10**) were easily prepared by reaction of the dichloro complexes **5** and **6** with 2 equiv. of methylmagnesium chloride in THF and isolated as yellow solids by crystallization from their hexane solutions. They were identified by chemical analyses and NMR spectroscopy.



Scheme 1.



Scheme 2.

Treatment of complexes **4**–**6** and **7** with 2 equiv. of $Mg(CH_2Ph)Cl$ in THF afforded the dibenzyl complexes $[M(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SiMe_2^tBu)(CH_2Ph)_2]$ (M = Ti **11**, Zr **12**, Hf **13**) and $[Zr(\eta^5\text{-}C_5H_4SiMe_2^tBu)_2(CH_2Ph)_2]$ (**14**). Pure products were obtained as red (**11**), orange (**12**) and yellow (**13**) solids and a waxy oil (**14**) respectively and their formulation is consistent with the analytical and spectroscopic NMR data (see Section 4). An analogous reaction of the zirconocene dichloride (**5**) with 1 equiv. of $Mg(CH_2Ph)Cl$ in THF afforded the monobenzyl compound $[Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SiMe_2^tBu)(CH_2Ph)Cl]$ (**15**) as an orange solid, after crystallization from hexane at −30 °C.

All of the dimethyl (**9**, **10**) and dibenzyl (**11**–**14**) compounds and the monobenzylzirconium derivative **15** are soluble in toluene and hexanes and their solutions were moisture and oxygen sensitive, being easily hydrolyzed in the presence of traces of water. However, all could be stored as solids unaltered for long periods under an inert atmosphere. Controlled hydrolysis of complex **15** by addition of stoichiometric amounts of water to its toluene solution afforded the μ-oxo dinuclear complex $[Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SiMe_2^tBu)Cl]_2(\mu\text{-}O)]$ (**16**), which was isolated as an orange crystalline solid and characterized by analysis, NMR spectroscopy and X-ray diffraction methods.

All of the alkyl compounds (**9**–**15**) were thermally stable when heated to 80 °C, although the dibenzyl complexes (**11**–**13**) produced small amounts of dibenzyl after prolonged heating (4 h). There were no signs that the *tert*-butyl group became active under these conditions [7]. With the aim of checking the effect of a bulkier alkyl group we tried to isolate the neophyl derivatives. Pure samples of the titanium derivative could not be obtained although elimination of *tert*-butylbenzene was not observed. Treatment of the zirconium complex **5** with 2 equiv. of neophyl lithium in THF afforded the dialkyl zirconium complex $[Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SiMe_2^tBu)(CH_2CMe_2Ph)_2]$ (**17**), which was isolated as a yellow solid after recrystallization from hexane at −35 °C and characterized by analytical and spectroscopic NMR data (see Section 4). Compound **17** was also thermally stable when heated to 80 °C and prolonged heating caused decomposition without activating the *tert*-butyl substituent.

Following a well-known method we used ^1H NMR spectroscopy to monitor the generation of the cationic species by addition of 1 equiv. of $B(C_6F_5)_3$ to a CD_2Cl_2 solution of **12** in a sealed NMR tube at −78 °C. The NMR spectrum recorded in CD_2Cl_2 at −80 °C showed the characteristic resonances of non-coordinated $[(CH_2Ph)B(C_6F_5)_3]^-$ (δ 2.74) and demonstrated the formation of the cationic species $[Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SiMe_2^tBu)_2(CH_2Ph)]^+$ (**12**$^+$) (see Section 4). Reversible dynamic behaviour was observed for **12**$^+$ between −80 and 0 °C with the coalescence temperature at −60 °C.

The base-free complex **12**$^+$ is stable at low temperature and decomposes at room temperature by reaction with the solvent CD_2Cl_2 to give the dichloro derivative. Compared with previously reported zirconium complexes [7] this cationic species **12**$^+$ does not activate the *tert*-butyl C–H which would give a metallacyclic species.

2.1. Structural studies

All of the dichloro (**4**–**8**) and dialkyl (**9**–**14**, **17**) symmetric and mixed metallocene complexes have C_{2v} and C_s symmetry respectively with their ^1H NMR spectra showing the two multiplets typically expected for the AA′BB′ spin system of the *tert*-butylsilyl-substituted cyclopentadienyl ring, and one singlet for the unsubstituted cyclopentadienyl ring. One additional singlet is observed for both equivalent methyl groups of the dimethyl derivatives **9**, **10** whereas the diastereotopic hydrogens of the benzyl **11**–**13**, and neophyl **17** complexes give rise to a characteristic doublet of doublets. In addition, the diastereotopic methyl groups of the neophyl **17** complex are observed as two singlets. However, only one singlet is observed for all four equivalent methylenic hydrogens of the C_{2v} symmetric dibenzyl complex **14**. The μ-oxo dinuclear zirconium complex **16** and the mono-benzyl mixed metallocene **15** are chiral molecules with ^1H NMR spectra showing the expected four multiplets for a ABCD spin system of the substituted cyclopentadienyl ring and the typical doublet of doublets for the diastereotopic methylenic hydrogens of the benzyl (**15**) groups.

Suitable crystals of complex **4** were obtained by very slow evaporation of its toluene solution at room temperature under nitrogen atmosphere. A view of the molecular structure is shown in Fig. 1 together with the

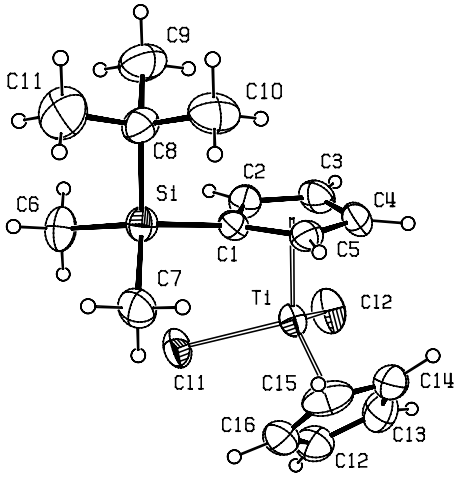


Fig. 1. Perspective view of the compound $[Ti(\eta^5\text{-}C_5H_4SiMe_2^tBu)(\eta^5\text{-}C_5H_5)Cl_2]$ (**4**).

Table 1
Selected bond lengths (Å) and bond angles (°) for **4**

Bond lengths			
Ti–Cl(1)	2.344(1)	Ti–Cl(2)	2.385(1)
Ti–CE(1)	2.060(4)	Ti–CE(2)	2.050(5)
Ti–C(1)	2.418(4)	Ti–C(12)	2.348(5)
Ti–C(2)	2.390(4)	Ti–C(13)	2.359(5)
Ti–C(3)	2.378(4)	Ti–C(14)	2.357(5)
Ti–C(4)	2.333(4)	Ti–C(15)	2.357(5)
Ti–C(5)	2.373(4)	Ti–C(16)	2.366(5)
Si–C(1)	1.885(4)	Si–C(7)	1.858(4)
Si–C(6)	1.863(4)	Si–C(8)	1.889(4)
Bond angles			
Cl(1)–Ti–CE(1)	107.6(1)	Cl(1)–Ti–CE(2)	106.7(1)
Cl(2)–Ti–CE(1)	106.4(1)	Cl(2)–Ti–CE(2)	106.0(1)
Cl(1)–Ti–Cl(2)	92.15(5)	CE(1)–Ti–CE(2)	131.1(2)

CE(1) and CE(2) are the centroids of the C(1)–C(5) and C(12)–C(16) cyclopentadienyl rings, respectively.

Table 2
Selected bond lengths (Å) and bond angles (°) for **16**

Bond lengths			
Zr–O	1.9520(6)	Zr–Cl	2.4723(11)
Zr–CE(1)	2.228(3)	Zr–CE(2)	2.233(4)
Zr–C(1)	2.559(3)	Zr–C(12)	2.511(3)
Zr–C(2)	2.536(3)	Zr–C(13)	2.507(3)
Zr–C(3)	2.533(3)	Zr–C(14)	2.544(3)
Zr–C(4)	2.489(3)	Zr–C(15)	2.542(3)
Zr–C(5)	2.539(3)	Zr–C(16)	2.546(3)
Si–C(1)	1.877(3)	Si–C(7)	1.871(5)
Si–C(6)	1.863(4)	Si–C(8)	1.903(4)
Bond angles			
Cl–Zr–CE(1)	107.56(9)	Cl–Zr–CE(2)	106.69(9)
O–Zr–CE(1)	107.26(8)	O–Zr–CE(2)	105.54(9)
O–Zr–Cl	97.51(5)	CE(1)–Zr–CE(2)	128.11(12)
Zr–O–Zr′	172.24(15)		

CE(1) and CE(2) are the centroids of the C(1)–C(5) and C(12)–C(16) cyclopentadienyl rings, respectively.

atomic numbering system. Selected bond distances and angles are given in Table 1.

The Ti atom is surrounded by two terminal chlorine atoms, a η^5-Cp and a η^5-$C_5H_4SiMe_2^tBu$ ligand and the coordination can be described as tetrahedral if the two centroids of the Cp rings are considered as coordination sites. The Ti–Cl(2) bond length is significantly longer than the Ti–Cl(1) one. Nevertheless these values fall in the range [2.317–2.386 Å] found in other mononuclear titanocene dichloro derivatives containing at least a Cp–SiR_3 ligand, retrieved from a bibliographic search on the Cambridge Structural Database.

Single crystals of complex **16** appropriate for X-ray diffraction studies were obtained by cooling its hexane solution to −35 °C. A view of the molecular structure of **16** is shown in Fig. 2 together with the atomic numbering system. Selected bond distances and angles are given in Table 2.

The dinuclear complex, with the oxygen atom bridging the two zirconium atoms presents a crystallographic *C*2 symmetry with the twofold axis passing through the oxygen atom. The tetrahedral coordination of the zirconium atoms (if the two centroids of the Cp rings are considered as coordination sites) is completed by a terminal chlorine atom, a η^5-Cp and a η^5-$C_5H_4SiMe_2^tBu$ ligand. The metal is chiral and the complex depicted in Fig. 1 adopts a *R*,*R* configuration, even if in the crystals both enantiomers *R*,*R* and *S*,*S* are present (the space group being centrosymmetric). The Zr–O and the Zr–Cl bond distances [1.9520(6) and 2.4723(11) Å, respectively] are in the range [Zr–O 1.942–1.959 Å] [10–13], [Zr–Cl 2.436–2.480 Å] [11,12] found in other μ-oxo-zirconocene derivatives. In the η^5-$C_5H_4SiMe_2^tBu$ ligand the Si atom is out of the Cp ring of 0.325(1) Å on the opposite site of the Zr atom and the bulky ^{t}Bu group is in an axial conformation with respect to the Cp ring (C(8)–Si–C(1)–C(2)) = (92.4(3)°), similar values were found also for **4** (0.321(1) Å and 89.6(3)°). The Zr–O–Zr′ bridge is almost linear (the angle is 172.24(15)°), as

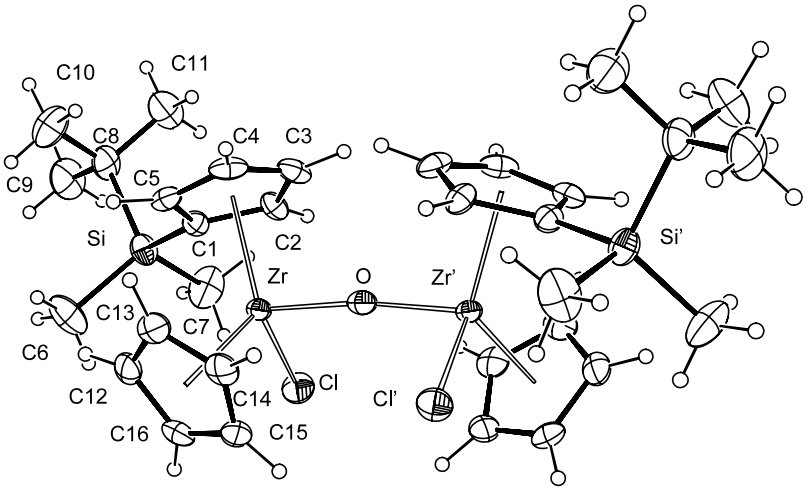


Fig. 2. Perspective view of the compound [{Zr(η^5-$C_5H_4SiMe_2^tBu$)(η^5-C_5H_5)Cl]$_2$}(μ-O)] (**16**).

found in the previously mentioned μ-oxo-zirconocene derivatives (values in the range 159.6–180°) [10–13].

2.2. Ethylene polymerization studies

The catalytic activity of the titanium (**4**), zirconium (**5**, **7**) and hafnium (**6**) dichloro complexes in ethylene polymerization was investigated using methylalumoxane (MAO) as cocatalyst at 21 °C under 1 atm. of ethylene. As expected, the hafnium complex **6** was not active whereas the symmetrical zirconium complex **7** with two more bulky *tert*-butylsilyl substituted rings showed an activity of 1.4×10^6 g PE (mol cat. h)$^{-1}$, higher than that found for bulkier substituted rings [6] and similar to that observed for the titanium derivative **4** with only one substituted ring (1.3×10^6 g PE (mol cat. h)$^{-1}$). The activity of the related less crowded mixed zirconocene **5** was slightly higher (1.9×10^6 g PE (mol cat. h)$^{-1}$) but lower than that reported for the related [Zr($C_5H_4SiMe_3$)$CpCl_2$] complex used as a reference (12.8×10^6 g PE (mol cat. h)$^{-1}$), indicating the steric influence of the bulky *tert*-butyl substituent.

3. Conclusions

New dichloro metallocene-type Group 4 metal complexes containing *tert*-butylsilyl-substituted cyclopentadienyl ligands have been successfully isolated and alkylated to give dimethyl, dibenzyl and neophyl compounds. All have been thoroughly characterized by chemical analysis and ^{1}H and ^{13}C NMR spectroscopy. No activation of the *tert*-butyl C–H bonds was observed under any conditions and the alkyl complexes were thermally stable. The mixed metallocene dibenzyl zirconium complex reacts with the Lewis acid $B(C_6F_5)_3$ at −80 °C to generate a mononuclear cationic species, which shows dynamic behaviour between −80 and 0 °C with the coalescence temperature at −60 °C. The dichloro metallocene complexes activated with MAO were used as catalysts for ethylene polymerization. The zirconium derivatives were the most active species although their activities are significantly lower than that observed for the less crowded [Zr($C_5H_4SiMe_3$)$CpCl_2$].

4. Experimental

All manipulations were performed either under argon using Schlenk techniques or in a glovebox. Solvents were purified by distillation from an appropriate deoxygenated drying agent (sodium for toluene and THF and sodium/potassium alloy for hexane). *n*-BuLi (1.6 M hexane), BzMgCl (2 M THF), MeMgCl (3 M diethylether), $ClSiMe_2^tBu$, $TlOC_2H_5$, $HfCl_4$ and $ZrCl_4$ were obtained commercially and used without purification. $Zr(\eta^5\text{-}C_5H_5)Cl_3\cdot DME$, $Hf(\eta^5\text{-}C_5H_5)Cl_3\cdot DME$ [14], $ZrCl_4(THF)_2$ [15] and $B(C_6F_5)_3$ [16] were prepared by reported methods. $LiCH_2CMe_2Ph$ was prepared as a yellow microcrystalline solid by reaction of lithium metal with $ClCH_2CMe_2Ph$ (Aldrich) in hexane under reflux for one week. ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity FT-300 and Varian Unity FT-500 Plus instruments, and chemical shifts were measured relative to residual ^{1}H and ^{13}C resonances of the deuterated solvents C_6D_6 ($\delta = 7.15$ pm), $CDCl_3$ ($\delta = 7.24$ pm) and C_6D_6 ($\delta = 128.0$ pm), $CDCl_3$ ($\delta = 77.0$ pm), respectively. C, H analyses were run on a Perkin–Elmer 240 microanalyzer.

4.1. Synthesis of $C_5H_5SiMe_2^tBu$ (*1*)

A solution of $ClSiMe_2^tBu$ (6.93 g, 46 mmol) in THF (30 ml) was added to a solution of C_5H_5Na (4.05 g, 46 mmol) in THF (40 ml)/hexane (70 ml) and the mixture was stirred for 2 days at room temperature (r.t.). The solvents were removed in vacuo and the residue was extracted into hexane (2 × 50 ml). After evaporation of the solvent the residue was redisolved in hexane (40 ml), filtered and dried under vacuum to give **1** as a brown oily solid (5,72 g, 31,7 mmol, 69%). ^{1}H NMR: (C_6D_6, 25 °C, 300 MHz): δ 0.13 (s, 6H, Si*Me*$_2$), 0.91 (s, 9H, *CMe*$_3$), 3.54 (m, 1H, Cp–H_{allyl}), 6.55, 6.57(2m, 4H, C_5H_4).

4.2. Synthesis of Li[$C_5H_4SiMe_2^tBu$] (*2*)

A solution of **1** (5,10 g, 28.3 mmol) in hexane (50 ml) was treated at −78 °C with a 1.6 M hexane solution of Li^{n}Bu (18.0 ml, 28.8 mmol). The mixture was allowed to warm to r.t. and stirred for 3 h until gas evolution had completely ceased. The solvent was removed in vacuo and the resulting white solid was washed with hexane and dried under vacuum to be identified as **2** (5,01 g, 26.9 mmol, 95%). ^{1}H NMR: ($C_5D_5N + C_6D_6$, 25 °C, 300 MHz): δ 0.38 (s, 6H, Si*Me*$_2$), 1.17 (s, 9H, *CMe*$_3$), 6.61, 6.62(2m, 4H, C_5H_4).

4.3. Synthesis of Tl[$C_5H_4SiMe_2^tBu$] (*3*)

$TlOC_2H_5$ (4.24 g, 17.0 mmol) was added at 0 °C to a diethylether (70 ml) solution of the cyclopentadiene **1** (3.07 g, 17.0 mol). The mixture was allowed to warm to r.t. and stirred for 1 day. After the solvent was evaporated, the resulting solid was washed with hexane and dried under vacuum to be characterized as the title compound (2.20 g, 12.2 mmol, 72%). *Anal.* Calc. for $C_{11}H_{19}SiTl$: C, 34.43; H, 4.99. Found: C, 33.83; H, 5.16%.

4.4. Synthesis of [Ti(η^5-$C_5H_4SiMe_2^tBu$)(η^5-C_5H_5)Cl_2] (**4**)

Toluene (50 ml) was added to a mixture of **3** (1.00 g, 2.6 mmol) and [Ti(η^5-C_5H_5)Cl_3] (0.57 g, 2.6 mmol) at r.t. The mixture was heated under reflux for 4 h and then cooled to ambient temperature. After filtration to separate TlCl, the red solution was concentrated and cooled to −40 °C to give **4** as a red solid which was filtered, washed with hexane and dried under vacuum (0.58 g, 1.6 mmol, 62%). *Anal.* Calc. for $C_{16}H_{24}SiTiCl_2$: C, 52.91; H, 6.66. Found: C, 52.41; H, 6.53%. ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 0.31 (s, 6H, Si*Me*$_2$); 0.79 (s, 9H, C*Me*$_3$); 6.54 (s, 5H, C_5H_5); 6.62 (t, 2H, $J = 2.4$ Hz, C_5H_4); 6.83 (t, 2H, $J = 2.4$ Hz, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, 300 MHz): δ −5.7 (Si*Me*$_2$); 17.6 (*C*Me$_3$); 26.5 (C*Me*$_3$); 120.2 (C_5H_5); 121.1 (C_5H_4); 121.6 (C_5H_4 *ipso*); 128.8 (C_5H_4).

4.5. Synthesis of [Zr(η^5-$C_5H_4SiMe_2^tBu$)(η^5-C_5H_5)Cl_2] (**5**)

THF (150 ml) was added at −78 °C to a mixture of **2** (1.14 g, 6.1 mmol) and [Zr(C_5H_5)Cl_3·DME] (2.15 g, 6.1 mmol). The mixture was allowed to warm slowly to r.t. and then stirred for an additional 6 h. After the solvent was removed under vacuum, the residue was extracted into toluene (50 ml). The solvent was evaporated to give **5** as a beige solid which was washed with hexane and dried under vacuum. (1.63 g, 4.0 mmol, 65%). *Anal.* Calc. for $C_{16}H_{24}SiZrCl_2$: C, 47.27; H, 5.95. Found: C, 47.72; H, 5.80%. ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 0.40 (s, 6H, *SiMe*$_2$); 0.76 (s, 9H, *CMe*$_3$); 5.92 (t, 2H, $J =$ 2.3 Hz, C_5H_4); 5.94 (s, 5H, C_5H_5); 6.34 (t, 2H, $J = 2.3$ Hz, C_5H_4). ^{1}H NMR ($CDCl_3$, 25 °C, 500 MHz): δ 0.32 (s, 6H, Si*Me*$_2$); 0.77 (s, 9H, C*Me*$_3$), 6.44 (s, 5H, C_5H_5), 6.55 (t, 2H, $J = 2.4$ Hz, C_5H_4); 6.68 (t, 2H, $J = 2.4$ Hz, C_5H_4). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 300 MHz): δ −5.7 (Si*Me*$_2$); 17.5 (*C*Me$_3$); 26.5 (C*Me*$_3$); 115.8 (C_5H_5); 116.4 (C_5H_4); 124.1 (C_5H_4 *ipso*); 125.3 (C_5H_4).

4.6. Synthesis of [Hf(η^5-$C_5H_4SiMe_2^tBu$)(η^5-C_5H_5)Cl_2] (**6**)

Following the same procedure described for **5**, [Hf(C_5H_5)Cl_3·DME] (1.58 g, 3.6 mmol) and **2** (0.67 g, 3.6 mmol) were reacted to give a grey solid which was characterized as **6** (1.04 g, 2.1 mmol, 58%). *Anal.* Calc. for $C_{16}H_{24}SiHfCl_2$: C, 38.91; H, 4.90. Found: C, 38.65; H, 4.81%. ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 0.32 (s, 6H, Si*Me*$_2$); 0.76 (s, 9H, *CMe*$_3$); 6.34 (s, 5H, C_5H_5); 6.45 (t, 2H, $J = 2.4$ Hz, C_5H_4); 6.59 (t, 2H, $J = 2.4$ Hz, C_5H_4). ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 0.39 (s, 6H, *SiMe*$_2$); 0.76 (s, 9H, *CMe*$_3$); 5.87 (m, 7H, C_5H_4 and C_5H_5); 6.26 (t, 2H, $J = 2.4$ Hz, C_5H_4). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 300 MHz): δ −5.6 (Si*Me*$_2$); 17.6 (*C*Me$_3$); 26.5 (C*Me*$_3$); 114.4 (C_5H_5); 115.3 (C_5H_4); 121.8 (C_5H_4 *ipso*); 124.2 (C_5H_4).

4.7. Synthesis of [Zr(η^5-$C_5H_4SiMe_2^tBu$)$_2Cl_2$] (**7**)

The same procedure described for **5** was followed using **2** (1.08 g, 5.8 mmol) and [$ZrCl_4(THF)_2$] (1.09 g, 2.9 mmol) to give a beige solid characterized as **7** (1.17 g, 2.4 mmol, 78%). *Anal.* Calc. for $C_{22}H_{38}Si_2ZrCl_2$: C, 50.73; H, 7.35. Found: C, 50.28; H, 7.16%. ^{1}H NMR (C_6D_6, 25 °C, 200 MHz): δ 0.44 (s, 12H, Si*Me*$_2$); 0.77 (s, 18H, C*Me*$_3$); 5.99 (t, $J = 2.5$ Hz, 4H, C_5H_4); 6.41 (t, $J = 2.4$ Hz, 4H, C_5H_4). ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 0.32 (s, 6H, Si*Me*$_2$); 0.76 (s, 9H, C*Me*$_3$); 6.50 (t, $J = 2.5$ Hz, 4H, C_5H_4); 6.64 (t, $J = 2.4$ Hz, 4H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, 300 MHz): δ −5.9 (Si*Me*$_2$); 17.4 (*C*Me$_3$); 26.3 (C*Me*$_3$); 116.2 (C_5H_4); 124.1 (C_5H_4 *ipso*); 125.8 (C_5H_4).

4.8. Synthesis of [Hf(η^5-$C_5H_4SiMe_2^tBu$)$_2Cl_2$] (**8**)

The same procedure described for **5** was followed using **2** (1,42 g, 7,6 mmol) and $HfCl_4$ (1.22 g, 3.8 mmol) to give **8** as a grey solid. (1.30 g, 2.13 mmol, 56%). *Anal.* Calc. for $C_{22}H_{38}Si_2HfCl_2$: C, 43.45; H, 6.30. Found: C, 43.32; H, 6.16%. ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 0.32 (s, 12H, Si*Me*$_2$); 0.76 (s, 18H, C*Me*$_3$); 6.41 (m, 4H, C_5H_4); 6.55 (m, 4H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, 500 MHz): δ −5.9 (Si*Me*$_2$); 17.5 (*C*Me$_3$); 26.3 (C*Me*$_3$); 115.1 (C_5H_4); 121.7 (C_5H_4 *ipso*); 124.6 (C_5H_4).

4.9. Synthesis of [M(η^5-$C_5H_4SiMe_2^cBu$)(η^5-C_5H_5)Me_2] (Zr **9**, Zr **10**)

The dimethyl complexes **9** and **10** were obtained by addition of a 3 M diethylether solution of MgMeCl to THF solutions of **5** and **6**, respectively at −78 °C. The reaction mixture was stirred for 6 h while it was warmed to r.t. The solvent was removed under vacuum and the residue was extracted into hexane. After the solvent was evaporated under vacuum, the complexes were obtained as waxy oils which were crystallized by cooling their hexane solutions at −45 °C.

Complex **5** (0.85 g, 2.1 mmol) in THF (50 ml) and MeMgCl (1.5 ml, 4.5 mmol) gave **9** as a yellow solid (0.54 g, 1.47 mmol, 70%). *Anal.* Calc. for $C_{18}H_{30}SiZr$: C, 59.11; H, 8.27. Found: C, 58.88; H, 8.16%. ^{1}H NMR (C_6D_6, 25 °C, 200 MHz): δ −0.08 (s, 6H, Zr*Me*$_2$); 0.12 (s, 6H, Si*Me*$_2$); 0.85 (s, 9H, C*Me*$_3$); 5.79 (s, 5H, C_5H_5); 5.95 (2m, 4H, C_5H_4). ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ −0.40 (s, 6H, Zr*Me*$_2$); 0.15 (s, 6H, Si*Me*$_2$); 0.81 (s, 9H, C*Me*$_3$); 6.06 (s, 5H, C_5H_5); 6.21 (t, 2H, $J =$ 2.3 Hz, C_5H_4); 6.24 (t, 2H, $J = 2.3$ Hz, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, 300 MHz): δ −5.8 (Si*Me*$_2$); 17.5 (*C*Me$_3$); 26.4 (C*Me*$_3$); 30.1 (Zr*Me*$_2$); 110.4 (C_5H_5); 114.2 (C_5H_4); 116.1 (C_5H_4 *ipso*); 117.5 (C_5H_4).

Complex **6** (0.99 g, 2.0 mmol) in THF (40 ml) and MeMgCl (1.35 ml, 4.0 mmol) gave **10** as a yellow solid (0.68 g, 1.5 mmol, 75%). *Anal.* Calc. for $C_{18}H_{30}SiHf$: C, 47.72 ; H, 6.67 . Found: C, 47.52; H, 6.75%. ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ −0.60 (s, 6H, HfMe_2), 0.16 (s, 6H, SiMe_2), 0.80 (s, 9H, CMe_3), 5.99 (s, 5H, C_5H_5), 6.16 (2m, 4H, C_5H_4). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 300 MHz): δ −5.7 (SiMe_2); 17.7 (*C*Me$_3$); 26.6 (CMe_3) 37.1 (HfMe_2), 110.1 (C_5H_5), 110.3 (C_5H_4), 113.8 (C_5H_4 *ipso*), 117.5 (C_5H_4).

4.10. Synthesis of [M(η^5-$C_5H_4SiMe_2^tBu$)(η^5-C_5H_5)($CH_2C_6H_5$)$_2$] (M = Ti **11**, Zr **12**, Hf **13**), [Zr(η^5-$C_5H_4SiMe_2^tBu$)$_2$($CH_2C_6H_5$)$_2$] (**14**), [Zr(η^5-$C_5H_4SiMe_2^tBu$)(η^5-C_5H_5)($CH_2C_6H_5$)Cl] (**15**) and [Zr(η^5-$C_5H_4SiMe_2^tBu$)(η^5-C_5H_5)($CH_2CMe_2C_6H_5$)$_2$] (**17**)

A 2 M THF solution of MgBzCl was added at −78 °C to THF solutions of the dichloro complexes **4**–**7**. The mixture was stirred for 1 h while it was warmed to r.t. The solvent was removed under vacuum and the residue was extracted into hexane. After concentration under vacuum, the complexes were crystallized by cooling their hexane solutions at −35 °C.

Complex **4** (1.30 g, 3.6 mmol) in THF (30 ml) and BzMgCl (3.6 ml, 7.2 mmol) gave complex **11** as a red solid (1.09 g, 2.3 mmol, 64%). The product must be protected from light because it is light sensitive. *Anal.* Calc. for $C_{30}H_{38}SiTi$: C, 75,92; H, 8.07. Found: C, 76.24; H, 8.22. ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 0.06 (s, 6H, SiMe_2); 0.81 (s, 9H, CMe_3); 1.76 (d, J = 10.0Hz, 2H, TiCH_2); 2.03 (d, J = 10.0Hz, 2H, TiCH_2); 5.93 (s, 5H, C_5H_5); 6.19 (t, J = 2.4 Hz, 2H, C_5H_4); 6.30 (t, J = 2.4 Hz, 2H, C_5H_4); 7.12–7.19 (m, 10H, CH_2Ph).

Complex **5** (1.00 g, 2.5 mmol) in THF (50 ml) and MgBzCl (2.5 ml, 5.0 mmol) gave complex **12** as an orange solid (0.98 g, 1.9 mmol, 76%). *Anal.* Calc. for $C_{30}H_{38}SiZr$: C, 69.57; H, 7.40. Found: C, 70.34; H, 7.46%. ^{1}H NMR (C_6D_6, 25 °C, 200 MHz): δ 0.03 (s, 6H, SiMe_2); 0.75 (s, 9H, CMe_3); 1.89 (2m, 4H, ZrCH_2); 5.66 (s, 5H, C_5H_5); 5.78 (t, J = 2.4 Hz, 2H, C_5H_4); 5.88 (t, J = 2.4 Hz, 2H, C_5H_4); 6.94 (m, 6H, o-p-C_6H_5); 7.25 (m, 4H, m-C_6H_5). ^{1}H NMR ($CDCl_3$, 25 °C, 500 MHz): δ 0.18 (s, 6H, SiMe_2); 0.77 (s, 9H, CMe_3); 1.83 (2m, 4H, ZrCH_2); 5.88 (s, 5H, C_5H_5); 6.08 (t, J = 2.4 Hz, 2H, C_5H_4); 6.16 (t, J = 2.4 Hz, 2H, C_5H_4); 6.91 (m, 6H, o-p-C_6H_5); 7.18 (m, 4H, m-C_6H_5).^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, 500 MHz): δ −5.7 (SiMe_2); 17.5 (*C*Me$_3$); 26.3 (CMe_3) ; 61.0 (Zr*C*H$_2$); 112.0 (C_5H_4 *ipso*); 112.3 (C_5H_5); 116.8 (C_5H_4); 120.1 (C_5H_4); 120.8 (p-C_6H_5); 125.5 (o-C_6H_5); 128.1 (m-C_6H_5); 152.4 (C_6H_5 *ipso*). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 300 MHz): δ −5.7 (SiMe_2), 17.6 (*C*Me$_3$); 26.4 (CMe_3); 61.5 (Zr*C*H$_2$); 112.6 (C_5H_5); 115.4 (C_5H_4 *ipso*); 117.2 (C_5H_4); 120.3 (C_5H_4); 121.3 (p-C_6H_5); 126.1 (o-C_6H_5); 128.5 (m-C_6H_5); 152.8 (C_6H_5 *ipso*).

Complex **6** (0.93 g, 1.9 mmol) in THF (40 ml) and MgBzCl (1.9 ml, 3.8 mmol) gave **13** as a yellow solid (0.79 g, 1.3 mmol, 68%). *Anal.* Calc. for $C_{30}H_{38}SiHf$: C, 59.54; H, 6.33. Found: C, 59.95; H, 6.52%. ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 0.06 (s, 6H, SiMe_2); 0.74 (s, 9H, CMe_3); 1.56 (d, J = 11.4 Hz, 2H, HfCH_2); 1.66 (d, J = 11.4 Hz, 2H, HfCH_2); 5.62 (s, 5H, C_5H_5); 5.76 (t, J = 2.8 Hz, 2H, C_5H_4); 5.82 (t, J = 2.8 Hz, 2H, C_5H_4); 6.94 (m, 4H, o-C_6H_5); 7.02 (m, 2H, p-C_6H_5); 7.28 (m, 4H, m-C_6H_5). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 300 MHz): δ -5.7 (SiMe_2); 17.7 (*C*Me$_3$); 26.4 (CMe_3); 65.4 (Hf*C*H$_2$); 111.8 (C_5H_5); 114.3 (C_5H_4 *ipso*); 116.1 (C_5H_4); 120.0 (C_5H_4); 121.7 (p-C_6H_5); 126.7 (o-C_6H_5); 128.3 (m-C_6H_5); 152.7 (C_6H_5 *ipso*).

Complex **7** (1.00 g, 1.9 mmol) in THF (30 ml) and MgBzCl (1.9 ml, 3.8 mmol) gave **14** as a waxy oil (0.78 g, 1.23 mmol, 65%). *Anal.* Calc. for $C_{36}H_{52}Si_2Zr$: C, 68.40; H, 8.29. Found: C, 68.03; H, 8.12%. ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 0.09 (s, 12H, SiMe_2); 0.77 (s, 18H, CMe_3); 1.95 (s, 4H, ZrCH_2); 5.93 (t, J = 2.5 Hz, 4H, C_5H_4); 6.05 (t, J = 2.4 Hz, 4H, C_5H_4); 6.93–6.99 (m, 6H, C_6H_5); 7.23–7.28 (m, 4H, C_6H_5). ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 0.17 (s, 12H, SiMe_2); 0.74 (s, 18H, CMe_3); 1.81 (s, 4H, ZrCH_2); 5.94 (t, J = 2.5 Hz, 4H, C_5H_4); 6.16 (t, J = 2.4 Hz, 4H, C_5H_4); 6.78–6.84 (m, 6H, C_6H_5); 7.13–7.18 (m, 4H, C_6H_5). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 300 MHz): δ −5.6 (SiMe_2); 17.7 (*C*Me$_3$); 26.4 (CMe_3); 63.0 (Zr*C*H$_2$); 116.6 (C_5H_4 *ipso*); 116.9 (C_5H_4); 120.9 (C_5H_4); 121.3 (p-C_6H_5); 125.9 (o-C_6H_5); 128.6 (m-C_6H_5); 153.6 (C_6H_5 *ipso*).

Complex **5** (1.60 g, 3.9 mmol) in THF (30 ml) and MgBzCl (1.9 ml, 3.9 mmol) gave **15** (1.10 g, 2.3 mmol, 61%) as orange crystals. The product is highly air and light sensitive. *Anal.* Calc. for $C_{23}H_{31}SiZrCl$: C, 59.76; H, 6.76. Found: C, 59,52, H, 6.53%. ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 0.18 (s, 3H, SiMe_2); 0.40 (s, 3H, SiMe_2); 0.79 (s, 9H, CMe_3); 2.18 (d, J = 11.7 Hz, 1H, ZrCH_2); 2.43 (d, J = 11.7 Hz, 1H, ZrCH_2); 5.39 (m, 1H, C_5H_4); 5.68 (s, 5H, C_5H_5); 5.73 (m, 1H, C_5H_4); 6.03 (m, 1H, C_5H_4); 6.28 (m, 1H, C_5H_4); 6.90–7.10 (m, 3H, C_6H_5); 7.28 (m, 2H, C_6H_5).

Complex **5** (1.34 g, 3.3 mmol) and $LiCH_2CMe_2Ph$ (0.93 g, 6.6 mmol) in THF (70 ml) gave **17** (1.44 g, 2.4 mmol, 73%) as a yellow microcrystalline solid. *Anal.* Calc. for $C_{36}H_{50}SiZr$: C, 71.81; H, 8.37. Found: C, 71.56; H, 8.39%. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ 0.19 (s, 6H, SiMe_2); 0.78 (s, 9H, CMe_3); 0.79 (d, J = 11.5 Hz, 2H, ZrCH_2); 1.03 (d, J = 11.5 Hz, 2H, ZrCH_2); 1.38 (s, 6H, CMe_2); 1.39 (s, 6H, CMe_2); 5.59 (s, 5H, C_5H_5); 5.73 (t, J = 2.5 Hz, 2H, C_5H_4); 5.82 (t, J = 2.5 Hz, 2H, C_5H_4); 7.14 (m, 2H p-C_6H_5); 7.28 (m, 4H, o-C_6H_5); 7.40 (m, 4H, m-C_6H_5). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 500 MHz): δ -5.3 (SiMe_2); 17.8 (*C*Me$_3$); 26.6 (CMe_3); 34.7 (CMe_2); 36.1 (CMe_2); 43.6 (*C*Me$_2$); 74.1 (Zr*C*H$_2$); 109.8

(C_5H_5); 113.0 (C_5H_4); 115.2 (C_5H_4 *ipso*); 118.9 (C_5H_4); 125.5 (p-C_6H_5); 126.2 (o-C_6H_5); 128.4 (m-C_6H_5); 152.3 (C_6H_5 *ipso*).

4.11. Synthesis of [{Zr(η⁵-C₅H₄SiMe₂ᵗBu)(η⁵-C₅H₅)Cl]₂}(μ-O)] (16)

Complex **15** (0.60 g, 1.3 mmol) was added to toluene (20 ml) containing water (12 μl, 0.66 mmol) and the mixture was stirred at r.t. for 4 h. After filtration the solvent was removed under vacuum and the residue extracted into hexane. Evaporation of the solvent and cooling at −35 °C gave yellow crystals of **16** (0.40 g, 0.5 mmol, 81%). A sample of **16** for X-ray diffraction was recrystallized from hexane. *Anal.* Calc. for $C_{32}H_{48}Si_2Zr_2Cl_2O$: C, 50.69; H, 6.38. Found: C, 50.45, H, 6.24%. ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 0.27 (s, 3H, SiMe_2); 0.37 (s, 3H, SiMe_2); 0.74 (s, 9H, CMe_3); 6.27 (s, 5H, C_5H_5); 6.34 (m, 1H, C_5H_4); 6.46 (2m, 2H, C_5H_4); 6.59 (m, 1H, C_5H_4).

4.12. NMR characterization of [Zr(η⁵-C₅H₄SiMe₂ᵗBu)-(η⁵-C₅H₅)(CH₂C₆H₅)]⁺ (12⁺)

CD_2Cl_2 was added at −78 °C to a mixture of equimolar amounts of complex **12** and $B(C_6F_5)_3$ in a NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy between 193 K and 273 K. ^{1}H NMR (CD_2Cl_2, 193 K, 500 MHz): δ 0.12 (s, 3H, SiMe_2); 0.27 (s, SiMe_2); 0.78 (s, 9H, CMe_3); 2.74 (sb, 2H, PhCH_2B); 3.00 (sb, 2H, ZrCH_2); 6.14 (s, 5H, C_5H_5); 6.38–7.50 (m, 14H, C_5H_4+*Ph*) ^{1}H NMR (CD_2Cl_2, 243 K, 500 MHz): δ 0.23 (s, 6H, SiMe_2); 0.80 (9H, CMe_3); 2.78 (b, 2H, PhCH_2B); 3.07 (bs, 2H, ZrCH_2); 6.16 (s, 5H, C_5H_5); 6.71–7.50 (m, 14H, C_5H_4+*Ph*).

4.13. X-ray structure determination of [Ti(η⁵-C₅H₄SiMe₂ᵗBu)(η⁵-C₅H₅)Cl₂] (4) and [{Zr(η⁵-C₅H₄SiMe₂ᵗBu)(η⁵-C₅H₅)Cl]₂}(μ-O)] (16)

Crystals of compound **4** and **16** were obtained by crystallization from toluene and hexane, respectively, and suitable sized crystals, under nitrogen atmosphere, in a Lindemann tube were mounted on a CAD4 diffractometer with graphite-monochromated Cu Kα radiation ($\lambda = 1.541838$ Å) The data were collected at 293 K for **4** and at 173 K (Oxford Cryosystems, 600 series Cryostream Cooler) for **16**. Crystallographic and experimental details are summarized in Table 3. A semi-empirical method of absorption correction was applied (maximum and minimum values for the transmission coefficient were 1.000 and 0.748 (**4**) and 1.000 and 0.807 (**16**)) [17]. No decay was observed for **4**, while a decay of 15% was observed during the data collection for **16**. The structures were solved by direct methods (SIR-92) [18] and refined by least-squares against F_o^2 (SHELXL-97) [19]. All the non-hydrogen atoms were refined anisotropically for both compounds. All the hydrogen atoms were introduced from geometrical calculations and refined using a riding model. All the calculations were carried out on the Digital AlphaStation 255 of the 'Centro di Studio per la Strutturistica Diffrattometrica del C.N.R.', Parma. The programs PARST [20] and ORTEP [21] were also used.

Table 3
Crystallographic data of **4** and **16** and details of the structure solutions and refinement procedures

Empirical formula	$C_{16}H_{24}Cl_2SiTi$	$C_{32}H_{48}Cl_2OSi_2Zr_2$
Formula weight	363.24	758.22
Temperature (K)	293(2)	173(2)
Wavelength (Å)	1.54184	1.54184
Crystal system, space group	triclinic, *P*-1	monoclinic, *C*2/*c*
Unit cell dimensions		
a (Å)	6.923(2)	13.401(6)
b (Å)	10.817(3)	7.857(4)
c (Å)	12.940(3)	35.286(9)
α (°)	70.51(2)	
β (°)	86.02(2)	101.01(2)
γ (°)	83.03(2)	
V (Å^3)	906.3(4)	3647(3)
Z	2	4
D_{calc} (Mg m^{-3})	1.331	1.381
Absorption coefficient (mm^{-1})	7.239	6.826
F(000)	380	1560
Crystal size (mm^3)	0.35 × 0.10 × 0.10	0.27 × 0.17 × 0.15
θ Range for data collection (°)	3.63–69.99	5.11–70.11
Index ranges	$-7 \le h \le 8$, $-12 \le k \le 13$, $0 \le l \le 15$	$-8 \le h \le 16$, $-7 \le k \le 9$, $-42 \le l \le 42$
Reflections collected/unique, R_{int}	3368/3368, 0.000	6613/3446, 0.0695
Data/restraints/parameters	3368/0/181	3446/0/182
Goodness-of-fit on F^2	0.769	1.048
Final *R* indices [$I > 2\sigma(I)$] (R_1, wR_2) [a]	0.0403, 0.0601	0.0372, 0.0949
R indices (all data) (R_1, wR_2) [a]	0.1208, 0.0787	0.0460, 0.1028
Largest difference peak and hole (e Å^{-3})	0.234 and −0.193	1.140 and −1.069

[a] GOOF = $[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}$, $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where $P = [\max(F_o^2,0)+2F_c^2]/3$.

4.14. Ethylene polymerization

All polymerization experiments were carried out in a 500 ml reactor charged with dry toluene and saturated bubbling ethylene for 30 m at 1 atm., purified, first over P_2O_5 and then through $AlMe_3$. Aliquots of toluene solutions of the cocatalyst MAO (MAO/catalyst = 1000/1) followed by the catalyst (4.4 μmol) were injected using a total volume of 100 ml of toluene. The pressure was maintained at 1 atm. and temperature at 21 °C during the polymerization experiment. After 5 min the reaction was quenched by addition of 5 ml of a methanol HCl

solution (5%). The suspensions were stirred for 24 h, filtrated and the polymer washed with methanol and dried at 70 °C for 24 h.

5. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 189194 and 189195 for compounds **4** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support of our work by MCyT (project MAT2001-1309) is gratefully acknowledged. R.W. and C.R. are grateful to DFG, MEC and Repsol S.A. for fellowships.

References

[1] (a) A. Togni, R.L. Halterman (Eds.), Metallocenes. Synthesis, Reactivity, Applications, vol. 2, Wiley–VCH, Weinheim, 1998;
(b) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. Engl. 34 (1995) 1143;
(c) M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255;
(d) G.G. Hlatky, Coord. Chem. Rev. 181 (1999) 256;
(e) H.G. Alt, A. Köppl, Chem. Rev. 100 (2000) 1205;
(f) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253.
[2] P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1.
[3] T. Cuenca, P. Royo, Coord. Chem. Rev. 193–195 (1999) 447.
[4] M.V. Galakhov, G. Heinz, P. Royo, Chem. Commun. (1998) 17.
[5] J. Cano, P. Royo, A. Tiripicchio, M.A. Pellinghelli, M. Lanfranchi, Angew. Chem., Int. Ed. Engl. 40 (2001) 2495.
[6] M. Bochmann, M.L.H. Green, A.K. Powell, J. Sassmannshausen, M.U. Triller, S. Wocadlo, J. Chem. Soc., Dalton Trans. (1999) 43.
[7] (a) J.I. Amor, T. Cuenca, M. Galakhov, P. Royo, J. Organomet. Chem. 497 (1995) 127;
(b) J.I. Amor, T. Cuenca, M. Galakhov, P. Gómez-Sal, A. Manzanero, P. Royo, J. Organomet. Chem. 535 (1997) 155.
[8] F. Amor, P. Royo, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 604 (2000) 126.
[9] S.K. Chaudhary, O. Hernandez, Tetrahedron Lett. 20 (1979) 99.
[10] T. Cuenca, P. Gomez-Sal, C. Martin, B. Royo, P. Royo, J. Organomet. Chem. 588 (1999) 134.
[11] M. Koyama, K. Kimura, M. Nakano, H. Yamazaki, Chem. Lett. (1998) 1139.
[12] K.P. Reddy, J.L. Petersen, Organometallics 8 (1989) 2107.
[13] G. Ciruelo, T. Cuenca, P. Gomez-Sal, A. Martin, P. Royo, J. Chem. Soc., Dalton Trans. (1995) 231.
[14] E.C. Lund, T. Livinghouse, Organometallics 9 (1990) 2426.
[15] L.E. Manzer, Inorg. Synth. 21 (1982) 135.
[16] A.G. Massey, A.J. Park, J. Organomet. Chem. 2 (1964) 245.
[17] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr., A 24 (1968) 351.
[18] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
[19] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Universität Göttingen, Göttingen, Germany, 1997.
[20] M. Nardelli, Comput. Chem. 7 (1983) 95.
[21] L. Zsolnai, H. Pritzkow, ZORTEP. ORTEP, Original Program Modified for the PC, Universität Heidelberg, Heidelberg, Germany, 1994.